

THE ANALYST.

DECEMBER, 1895.

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

THE monthly meeting of the Society was held on Wednesday, November 6, at the Chemical Society's Rooms, Burlington House, at eight p.m., the chair being occupied by the President (Dr. Stevenson).

The minutes of the previous meeting were read and confirmed.

The following gentlemen were elected. As Members: Robert William Atkinson, B.Sc. (Lond.), F.I.C., and J. Walter Leather, Ph.D., F.I.C. As Associate: Herbert Burgess, assistant to Dr. Graham.

The following gentlemen were proposed for election as Members of the Society: Thomas Hawkins Percy Heriot, Chemist to Messrs. Welford and Sons, Limited; Frank H. Leeds, F.I.C., F.C.S., Analytical and Consulting Chemist; Alex. K. Miller, Ph.D., Analytical Chemist; C. A. Mitchell, B.A., A.I.C., Chemist to Messrs. Beaufoy and Co.; C. H. R. Moore, F.I.C., Chemist to the Sheppey Glue and Chemical Works, Limited; Clarence Arthur Seyler, B.Sc. (Lond.), F.I.C., Public Analyst for the County of Carmarthen, and Deputy Public Analyst for the County of Glamorgan and the Borough of Swansea; Benjamin Watmough, Analyst at Messrs. Brotherton and Co.'s Ammonia Works, Wakefield.

NOTE ON A RECENT MILK CASE INVOLVING A SAMPLE OF ABNORMAL MILK,

By R. BODMER.

On April 4 I received a sample of milk from one of my Sanitary Inspectors which yielded the following analytical figures:

Specific gravity	...	...	...	...	1028.10
Total solids	...	...	...	...	10.85 per cent.
Fat	...	...	...	...	3.20 "
Solids-not-fat	...	...	...	...	7.65 "
Ash	...	...	...	...	0.66 "

I returned it as containing 10 per cent. of added water.

The vendor sent his sample to another analyst, who reported it as containing 8 or 9 per cent. of added water. The vendor then had a certain cow in his shed (which contained about twenty cows) milked in the presence of his analyst, and the milk was found by him to be *equivalent* to one containing about 8 per cent. of

added water. The Inspector's sample was sent to Somerset House, and was reported to contain "not less than 10 per cent. of added water."

The case did not, however, stop here. The vendor appealed to the magistrate at Southwark Police Court to permit a particular cow to be milked in the presence of the Chief Sanitary Inspector for the Bermondsey Vestry. Permission was granted; but the "appeal to the cow" only came off on June 13, more than two months after the taking of the original sample. Two cows were milked separately, Nos. 1 and 2, and samples taken from each. I was not present at the milking, but cautioned the Inspector to see that the cows were milked dry.

The figures of the analyses were as follows :

	No. 1.	No. 2.
Specific gravity	1024·80	1028·90
Total solids	10·38 per cent.	11·68 per cent.
Fat	3·14 "	3·48 "
Solids-not-fat	7·24 "	8·20 "
Ash	0·88 "	0·84 "

Thus, on the 8·5 basis, No. 1. was equivalent to milk containing 15 per cent. of added water, and No. 2 to milk containing 3 per cent. of water.

The *ash* yielded by both milks was extremely high, whereas the ash yielded by the original sample was *low*, and quite in accordance with the presence of added water.

I reported the two samples as being abnormal. On the case being again heard, I gave evidence, and maintained that the original sample was a watered, and not an abnormal, milk. Dr. Dyer also appeared in support of my certificate.

The analyst of the vendor, however, stated that, although he had previously reported that the original milk was *watered*, he now believed it to be *genuine*. He altogether disagreed with Dr. Dyer and myself that the ash was any guide in discriminating between a watered and an abnormal milk, and that 0·66 ash was quite compatible with a genuine milk.

The vendor's wife and his stableman gave evidence that the original milk came from *one cow* (No. 1), and that no water was added.

The cows were, I believe, shorthorns, and were chiefly fed on brewers' grains.

The magistrate decided to dismiss the case, but declined to grant the defendant costs against the Vestry.

I also determined the *milk-sugar* in the No. 1 sample. The full analysis of No. 1 milk was, therefore :

Fat	3·14 per cent.
Milk-sugar	2·59 "
Casein	3·77 "
Ash	0·88 "

This bears out Mr. Richmond's theory that in abnormal milks the *milk-sugar* is generally deficient. Other observers have also noted the high ash in abnormal milks.

DISCUSSION.

Mr. CASSAL thought that the only satisfactory way of dealing with cases such as these, in which the adulteration was carried on "at the other end of the cow," by

improper feeding, with or without improper management, was to make it perfectly plain that the so-called milk was in reality not milk at all, but merely a pathological fluid which could not be regarded as coming within the meaning of the term "milk" as it was understood by the public, and as it was used by a purchaser under the Sale of Food and Drugs Acts. This had been pointed out repeatedly by the speaker and others at the meetings of the Society, in Courts of Law, and elsewhere, and it was to be regretted that the necessity for stating so obvious a fact should arise so frequently. The statement, which he gathered had actually been made in Court, that a proper determination of the ash of milk did not afford evidence in regard to the presence of extraneous water was, of course, absolutely incorrect.

Mr. WYNTER BLYTH thought it very extraordinary that a magistrate should have attached so much importance to evidence which was obtained after a two months' interval, and which he would have imagined had hardly any bearing at all upon the real question at issue.

Mr. RICHMOND thought that the cause of the unsuitability of brewers' grains for cattle feeding when given alone was probably due, not so much to the large proportion of water which they contained, as to the acidity which developed in them after they had been kept in stock for some time, and which caused severe diarrhœa.

Mr. HEHNER said that the matter of natural abnormality had nothing to do with the main question, which turned upon the actual composition of the article which a purchaser was entitled to expect when he asked for milk. This was really the only safe basis that could be adopted. No excuse whatever ought to be accepted for deficiencies (whether natural or artificial) from a reasonable and lenient standard of composition.

Dr. DYER remarked that in milk adulteration cases a difficulty sometimes arose as to the specific charge made against the defendant. If the charge was that the article sold was not "of the nature, substance and quality demanded," the case could be easily dealt with; but if the charge merely referred to the addition or abstraction of any ingredient, a magistrate seemed to be more or less bound to consider such a case in its strictly legal aspect, and if he was satisfied that the article had not been tampered with, but was really abnormal, it was difficult to see how he could convict on a specific charge of addition or abstraction.

In the case alluded to by Mr. Bodmer, a conviction would probably have been obtained, but for the statement made by the analyst who appeared for the defendant that there was nothing necessarily abnormal in a high or low ash. This analyst also stated that the percentage of ash obtained would depend to a great extent upon the method employed for determining it, losing sight, apparently, of the fact that the determinations had been in this case made under the same conditions by the same analyst, and confessing that he had himself not determined the ash.

Brewers' grains were used as a staple article of food by most large milk-producers, and, properly employed, must be considered to be one of the best artificial foods that could be given to cows. The fact of their being sour was not detrimental to their feeding value; in proof of this he instanced the case of a large farmer and supplier of milk to the London market, whose farm he frequently visited. This gentleman had a large pit, or silo, which he filled up with brewers' grains when these

were plentiful, keeping them pressed down for future use. They were often kept for months before they were consumed, being perfectly sour, but the milk produced was always of good quality. Grains, however, were not relied upon alone, but were supplemented by a reasonable quantity of concentrated food, viz., cake and meal. Thus supplemented, grains were exceedingly useful in promoting a good flow of milk, but, in order that the milk might be of good quality, an adequate supply of concentrated food, in addition to the highly watery grains and other moist, bulky food, was absolutely necessary.

The PRESIDENT remarked that saline matter was often added to grains in order to counteract their insipidity. He knew from observation on the human being that saline matters administered internally tended to appear in the milk secretion, and if this were also the case with cows, it might offer some clue to the cause of the high percentages of ash in these milks, if the assumption was correct as to brewers' grains being the main item in the diet.

Mr. BODMER said that he was of the same opinion as Mr. Cassal regarding the proper meaning of the term "milk." Every effort was made to explain the matter clearly to the magistrate, but the evidence of the defendant's wife and stableman appeared to create a doubt in his mind, the benefit of which was given to the defendant. He had brought the matter before the Society mainly for the sake of pointing out the high percentage of ash and low milk-sugar in the abnormal milk, in the hope that it might lead to the possibility of discriminating between milk which was really abnormal and milk which had been watered.

NOTE ON TWO SAMPLES OF "FILLED" OR LARD CHEESE.

By R. BODMER.

DURING the discussion on a recent paper on Cheese by Messrs. Chattaway, Pearmain and Moor, Mr. Allen remarked that so far no samples of "filled" or lard cheese had come under his notice in this country. I have recently analysed two such adulterated cheeses which gave the following figures:

	No. 271, July, 1895.	No. 347, September, 1895.
Fat	42.4 per cent. ...	31.7 per cent.
Valenta test	60° C....	70° C.
Reichert figure (2.5 grammes)	0.9 c.c. $\frac{N}{10}$ baryta ...	0.8 c.c. $\frac{N}{10}$ baryta.
Insoluble fatty acids	...	9.35 per cent.
I reported: No. 271, Skim-milk cheese	...	60 per cent.
Fat other than butter-fat	...	40 per cent.
No. 347, Skim-milk cheese	...	70 per cent.
Fat other than butter-fat	...	30 per cent.

Both samples were, I believe, American cheeses, and in both cases the vendors were convicted and fined.

THE COMPOSITION AND ANALYSIS OF CONDENSED MILK.

By T. H. PEARMAIN AND C. G. MOOR, M.A.

CONDENSED milk appears to have been first prepared about the year 1856, and is now an article of great importance, more particularly on account of the immense quantity used in the feeding of young children.

We may divide the various brands sold in this country into four classes. Many of these brands are the same milk under different names: 1, unsweetened milks; 2, sweetened milks; 3, sweetened partly-skimmed milks; 4, sweetened skimmed milks.

In most cases the degree of concentration is that obtained by evaporating three volumes to one; that is, the addition of two volumes of water (to an unsweetened milk) will produce a strength equal to the original.

1. The unsweetened milks, of which there are at present six different brands, are all well prepared, and keep perfectly. They contain the due proportion of fat.

2. This class forms by far the largest and most important part of the whole supply, and for the most part there is nothing to complain of in them, except that the degrees of dilution recommended would in every case produce a milk below standard. A few of them have been prepared from milk partly deprived of its fat.

3. Many of these which are stated to be prepared from milk from which a portion of its fat has been removed, are almost entirely devoid of fat, containing less than 10 per cent. of the original fat.

4. Separated milks (miscalled skimmed milks) are largely used by poor and ignorant people for infant feeding, and there can be no doubt but that great harm results from this practice.

It is now becoming more generally recognised that by the use of condensed milks all danger of milk epidemics is avoided, which is an additional reason for the favour they enjoy in the feeding of children.

In the appended table of analyses will be noticed a sample of Italian condensed milk; this is not sold in small tins for ordinary use, but only in bulk to dairymen for diluting down and selling as fresh cows' milk. It is admittedly partly deprived of its fat, but is supposed to be capable of producing four times its volume of ordinary milk.

In the *British Medical Journal*, July 27, 1895, is a report by Dr. Dyer on seventeen samples of condensed milk, nearly all of which were skimmed or partly-skimmed milks. In his report some of the labels were reproduced, which is a feature of great interest, as it has had the effect of causing a fresh issue of labels.

In the present state of the law as interpreted by the judicial authorities, condensed skimmed milk, that is to say, milk deprived of its fat, in the absence of which it ceases to be milk in the true sense of the word, may lawfully be labelled "Condensed Milk," provided the fact is printed somewhere on the label in more or less microscopical type that the tin "contains skimmed milk." In other words, a manufacturer may condense skimmed milk and describe it in large letters on the body of the tin as "Condensed Milk," whereas an ordinary milk-vendor is fined for selling skimmed milk, unless the fact is stated at the time of purchase. Attention has already been called to this point in the *British Medical Journal* report.

It is very probable that the high infant death-rate, particularly among the poor, is largely due to, if not actually caused by, the use of these skimmed condensed milks, which subjects the children to a process of slow starvation. In our opinion, it is not only very desirable that the words "Skimmed" or "Separated" should be printed on the label in as large and prominent letters as the words "Condensed Milk," but we would go further, and say that the statement "Skimmed milk is unfit for the nourishment of children" should be made compulsory. This

statement is made on the label of one brand of skimmed milk, and the manufacturers should not be compelled to suffer for their honesty in pointing out what less honest makers are ready to conceal. In the case of one brand of condensed skimmed milk, it is actually recommended for children's use. Even in the case of sweetened whole milks, the amount of water recommended to be added to the contents of the tin to produce a product for "ordinary" purposes or for infant feeding is in nearly every case largely in excess of what it should be, as will be seen from the following table of examples taken at random from the table of analyses.

Sweetened Whole Milk.	Dilution recommended for Household Purposes.	Percentage of Fat in such Product.	Dilution recommended for Infants' Use.	Percentage of Fat in such Product.
A	1 to 3	2.6	1 to 5	1.8
B	1 to 5	1.6	1 to 14	0.7
C	1 to 5	1.6	1 to 14	0.6
D	1 to 6	1.4	1 to 15	0.7
E	1 to 5	2.1	1 to 14	0.8
F	1 to 5	1.7	1 to 14	0.7
G	1 to 5	1.7	1 to 14	0.7
Human milk	—	—	—	3.0

In the above cases the extreme dilution recommended on the label is taken. Thus, it will be seen that the dilutions recommended for children's use, except in one case, contain on the average less than one quarter the amount of fat they should contain when compared with human milk.

THE ANALYSIS OF CONDENSED MILK.

The contents of the tin are well mixed, and 10 grammes weighed into a beaker and made up to 100 c.c. We now have a 10 per cent. solution, which serves for the following estimations:

Total Solids.—20 c.c. of the solution are evaporated in a platinum dish. The milk solids take at least six hours to dry to constant weight.

Ash.—This is determined on the above by igniting at as low a temperature as possible.

Proteids.—10 c.c. of the solution are evaporated to dryness in a flask, and the nitrogen determined by the Kjeldahl process. The proteids are then calculated by the usual factor.

Milk-sugar.—10 c.c. of the solution are made up to 100 c.c. by the addition of 40 c.c. of water and 50 c.c. of ammonia. The milk-sugar is then determined in this 1 per cent. solution by Pavy's method.

Fat.—Two quantities of 5 c.c. of the solution are placed on two Adams' papers, well dried, and the coils extracted with anhydrous ether.

It is well known that the Werner-Schmidt process cannot be applied to condensed milks on account of the solubility of caramel in moist ether, which renders the Adams process the only accurate method available for the estimation of the fat. In view of the length of time taken by this process, we have made repeated attempts to determine the fat by the Leffmann-Beam machine. This, we are satisfied, can be

done with a fair amount of accuracy if the following details are adhered to in every respect, special attention being paid to the strength of the sulphuric acid. The great objection to this method is the large factor that has to be employed, namely, 15·5, seeing that we find it necessary to work on only 1 gramme of the original sample. The procedure is as follows: 10 c.c. of the 10 per cent. solution of the sample are run into the bottle, and 3 c.c. of the hydrochloric acid-fusel-oil mixture added, the bottle well shaken, and then 15 c.c. of sulphuric acid of 85·0 per cent. added with agitation. Sufficient of a hot mixture of sulphuric acid and water (1:2) is then added to the bottle to bring the top of the liquid nearly up to the zero mark. The bottle is then "whirled" in the machine for three minutes. The fat will not all come up at once, but after placing the bottle in the water-oven for two or three minutes, and again "whirling," the entire amount of fat will be obtained, which is then carefully measured off with a pair of dividers.

Respecting the relations of the fat, proteids and milk-sugar in condensed milk, it does not seem to be so constant as might be expected. We note a curious difference in the relations of these bodies in the unsweetened condensed milks we have examined when compared with some analyses published by Battershall ("Food Adulteration and its Detection," p. 53). These analyses show the fat, proteids and milk-sugar to be nearly equal, whereas it is customary to find these constituents to be in the ratio of 2 : 2 : 3.

In conclusion, we hope that the recent agitation in connection with fraudulent condensed milk will call attention to what may be termed, without exaggeration, a national question.

ANALYSES OF CONDENSED MILKS.

Brand.	Total Solids.	Fat.	Milk-sugar.	Pro-teids.	Ash.	Cane-sugar (by difference).	Description on Label on Tin.
Anglo-Swiss ...	74·4	10·8	16·0	8·8	1·7	37·1	Unskimmed.
Beehive ...	77·7	0·2	—	—	2·6	—	Skimmed.
Calf ...	58·0	1·0	16·0	7·5	1·6	31·9	Skimmed.
Cleaves ...	71·0	10·8	17·1	10·1	1·7	31·3	Not skimmed.
Clover-leaf ...	76·0	10·7	13·6	8·8	2·0	40·9	Guaranteed to contain all its original cream.
Cow ...	74·9	2·0	13·0	11·5	2·6	45·8	Partly skimmed.
Cowslip ...	70·9	1·4	14·6	11·4	1·6	41·9	Skimmed; guaranteed to be entirely pure.
Cradle ...	29·9	9·5	15·5	3·1	1·8	none	Humanized condensed milk.
Cross ...	75·0	1·2	16·0	10·5	2·6	44·7	Skimmed.
Cup ...	56·9	1·0	15·4	8·5	1·6	30·4	Skimmed.
Daily ...	68·8	1·3	13·7	10·2	2·5	41·1	Skimmed.
Daisy ...	64·0 ^e	0·5	—	—	2·2	—	Skimmed.
Darby and Joan ...	73·1	9·8	13·0	13·3	2·3	34·7	Contains nothing but full cream milk.
Drummer-boy ...	—	1·0	—	9·6	—	—	Skimmed.
Farmhouse ...	77·0	0·4	—	—	1·7	—	Skimmed.

ANALYSES OF CONDENSED MILKS—*continued.*

Brand.	Total solids.	Fat.	Milk-sugar.	Pro- teids.	Ash	Cane- sugar (by differ- ence).	Description on Label on Tin.
Favourite ...	70.6	0.3	—	10.0	2.1	—	Skimmed.
Fern ...	67.7	10.7	15.0	10.6	1.6	29.8	Quite genuine.
First Swiss ...	36.7	10.5	14.2	9.7	2.1	none	Unsweetened ; guaranteed pure and unskimmed.
Fourpenny ...	76.5	10.4	13.0	9.8	2.0	41.3	Not skimmed.
Full Weight ...	76.5	11.0	13.5	12.3	2.5	37.2	Not skimmed.
Geranium ...	75.0	9.8	13.0	7.5	1.6	43.1	Guaranteed perfectly pure.
Go-a-head ...	76.1	10.0	14.6	9.7	2.1	39.7	Guaranteed pure ; no part of the cream has been extracted.
Goat ...	71.0	1.2	12.0	9.9	2.0	45.9	Skimmed.
Golden Eagle ...	—	1.0	—	6.8	—	—	Guaranteed pure milk, from which a portion of the cream has been extracted.
Gowan ...	72.0	10.8	13.4	10.5	1.7	35.6	Partly skimmed.
Handy ...	75.5	0.3	17.0	12.3	1.6	44.3	Skimmed.
Hollandia ...	43.0	9.8	18.5	11.3	2.5	none	Best quality ; without sugar.
Home ...	71.3	1.3	12.5	11.1	2.5	43.9	Skimmed.
Home and Colonial	72.6	13.5	17.0	9.7	1.9	30.5	(No description on label.)
Household ...	70.0	0.3	—	—	2.0	—	Separated milk.
Ideal ...	38.0	12.4	16.0	8.3	1.7	none	Enriched with 20 per cent. of added cream (not sweetened).
Imperial Dairy ...	70.4	3.7	12.6	11.3	1.6	41.2	Skimmed.
Italian ...	44.6	9.5	16.5	14.7	3.5	none	Unsweetened ; sold for diluting down.
Lancer ...	67.6	0.3	16.6	12.3	2.6	35.8	Skimmed.
Lifeguard ...	65.8	0.3	—	—	2.4	—	Skimmed.
Lipton's ...	71.0	9.3	14.5	7.9	2.2	37.1	Prepared from the richest pure milk.
Lovers ...	73.0	0.2	—	—	2.1	—	Skimmed.
Lucerne Lion ...	71.7	10.8	15.2	9.3	2.0	34.4	Guaranteed finest quality (mountain milk).
Minstrel ...	75.3	0.2	15.4	9.7	1.7	48.3	Skimmed.
Mother ...	72.0	8.8	13.7	7.3	1.7	40.5	Guaranteed to be prepared with the best and richest cows' milk.
Milkmaid ...	76.3	11.0	14.6	9.7	2.3	38.7	Swiss ; genuine.
Nestlé's ...	77.2	13.7	15.0	9.7	1.6	37.2	Prepared from pure milk of Swiss cows.
Rose ...	76.6	12.4	17.6	8.3	2.2	36.1	Not skimmed.
Scandinavian ...	74.6	10.8	14.5	6.6	1.6	41.1	Perfectly pure.
Shamrock ...	71.6	0.5	18.4	11.8	2.0	38.9	Skimmed.
Springtime ...	74.0	0.3	—	—	2.2	—	Skimmed.
Tip-top ...	74.0	10.7	15.4	8.8	1.7	37.4	Not skimmed.
Viking ...	34.2	10.0	13.3	9.0	1.9	none	Unsweetened (full cream).
Wasp ...	73.4	1.0	12.3	11.0	1.9	47.2	Skimmed.
World's Tea Co. ...	75.0	9.3	—	—	2.0	—	Full cream.

DISCUSSION.

Dr. DYER said that, as some recently-published analyses made by him of condensed milk had been referred to, he would like to say that he had nothing to do with the selection of the various brands analysed, and really did not know how far they consisted of brands having a free sale, and how far of less common brands. He did not purchase the samples, but received them from the editor of the *British Medical Journal*, with an instruction to determine the fat and report the result.

Mr. RICHMOND said that many of the percentages of ash given in the table were distinctly lower than those which he had been accustomed to regard as normal to milk. Dr. Vieth had found that the amount of ash in milk was almost invariably about 8.3 per cent. of the solids-not-fat, and experiments which he (the speaker) had himself made completely confirmed the correctness of this proportion.

Mr. BEVAN said he would like to ask the authors if they were quite satisfied with the Adams method for fat determination. It seemed to him that in condensed milk the conditions were far from favourable to complete extraction of the fat.

Dr. DUPRÉ, referring to the statement made by the authors that condensed milk was free from all risk of imparting infectious diseases, said that he remembered a case in which an outbreak of scarlatina was distinctly traceable to some condensed milk which had been used, and in which Dr. Klein detected the micrococcus of scarlatina.

Mr. HEHNER remarked that all the milks referred to in the paper seemed to be correctly described as whole milks or skimmed milks on the labels. It was very important, however, to draw attention to the directions given as to the addition of water, which were in most cases entirely wrong. The "condensed milkman" (if the term might be used) appeared to be in an unfortunate position, since the addition of the proper proportion of water—namely, about 2 parts of water by weight to 1 of milk—resulted in a product which was an almost undrinkable syrup; while, if a sufficient quantity was added to make it palatable, the nitrogenous matters were reduced to a minimum. As a matter of fact, it was impossible to make from condensed milk anything that could be said to correspond with the original milk, and attempts to do so ought to be entirely discouraged. At the same time, the manufacture of skimmed or separated condensed milk was, in his opinion, a perfectly legitimate trade, and if the article was properly and plainly labelled, no normal objection could be raised against it. The proportions of ash found by the authors of the paper seemed to vary a great deal. He noticed one instance in which the proportion was 3.5 per cent., which would mean that the original milk, containing, say, 0.7 per cent., was condensed five times, provided that no other ash had been added. Others contained as little as 1.4 per cent. He could not help thinking that some error must have crept into these determinations.

The PRESIDENT remarked that, taking the average of the last twelve milks in Messrs. Pearmain and Moor's table, which were all that he had had time to critically examine, the ratio which the ash bore to the solids-not-fat agreed fairly well with the normal proportion. The average ratio between the ash and the proteids was also almost exactly normal. In fact, these last twelve cases seemed to bear out the assumption that the analyses had been fairly and correctly made.

Mr. MOOR, in reply to Mr. Bevan's question regarding the Adams process, said it was the most satisfactory method they had been able to find. They had tried the Leffmann-Beam process in eight or nine cases, and found it to work well, even when a large quantity of cane sugar was present, if the strength of the acid was strictly adhered to. As, however, the estimation could be made in about five minutes, this method seemed to be worthy of a more extended trial. In working the Adams process, it was their practice, after the extraction was finished, to dry the coil and go through the operation of extraction a second time, so as to make sure that all the fat was obtained. With regard to the question of disease propagation, the thermal death-point of nearly all disease organisms ranged between 50° and 60° C., and as the process of manufacture involved the raising of the milk to a temperature of 70° C. four successive times, it did not seem probable that any disease organisms could survive.

Dr. DUPRÉ pointed out that, although all mature disease organisms would be killed by the heat, spores of some of these organisms might still survive and develop in the condensed milk after the processes of manufacture had been completed.

Papers were read on the following subjects, the publication of which is unavoidably deferred: "Note on the Estimation of Minute Quantities of Metals in Liquids," by E. Russell Budden and H. Hardy; "Note on a convenient form of Polarimeter for examining Essential Oils," by E. Russell Budden.

NOTES ON COMMERCIAL CONDENSED MILKS.

BY ALFRED H. ALLEN.

IN the summer of 1894 I received, under the Sale of Food and Drugs Act, a fairly complete collection of the brands of condensed milk then in the market. The results obtained are interesting in connection with the paper of Messrs. Moor and Pearmain, as they show the change in practice of manufacturers of condensed milk since that date. The partially-skimmed milks which figure so largely in the table of results appended to this paper have now nearly disappeared from commerce, and it will be noted that the character of several of the brands analysed by Messrs. Moor and Pearmain and also by myself has materially changed. Another practice which it is well to bear in mind is that if, through proceedings in court or other circumstances, the quality of a brand of condensed milk is challenged, certain manufacturers simply rechristen the product, and reissue the old tins as some other brand.

As the proportion of fat in unskimmed milk is fully equal to, or somewhat in excess of, the proteids, a comparison of these two constituents affords a ready means of ascertaining whether any notable quantity of the cream natural to the milk has been removed.

With regard to the general character of condensed milk, while some few manufacturers prepare a first-rate article, for which they obtain a first-rate price, in other cases the statements made on the label are by no means borne out by the analyses. Particularly objectionable are the statements with respect to the amount of dilution

to be practised in order to restore the milk to its original concentration. As the amount of condensation is never more than 3 to 1, directions to dilute the milk with 6 to 8 parts of water, and for special purposes to add from 10 to 15 parts of water, are open to grave animadversion. It seems to be the case, however, that, as the law at present stands, there is no penalty under the Sale of Food and Drugs Act for attaching to an article a label bearing untrue statements or misleading directions. The practice might be dealt with under the Merchandise Marks Act, but with that enactment public analysts are not officially concerned.

Brand.	Total Solids.	Fat.	Proteids.	Description on Label.
Alderney ...	68·10	11·05	10·95	Guaranteed to contain 60 per cent. of original cream.
Anglo-Swiss ...	73·70	9·70	9·87	Best unskimmed country milk.
Arcadia ...	71·20	8·08	10·25	From best and purest cow's milk.
Calf ...	66·30	—	10·19	Contains skimmed milk.
Cow ...	72·50	6·50	10·57	From partly-skimmed milk.
Cowslip ...	72·10	0·18	10·20	Skimmed milk.
Daily ...	69·64	0·26	10·58	From skimmed milk.
Devon ...	70·60	8·50	10·63	From skimmed milk.
Farm ...	66·60	0·12	10·14	From skimmed milk.
First Swiss ...	28·37	8·76	10·14	Unsweetened.
First Swiss ...	36·10	11·06	12·75	Unsweetened.
Fourpenny ...	75·36	5·40	13·18	From pure fresh milk containing all its cream.
Full weight ...	75·70	11·60	11·27	Warranted not skimmed.
Geranium ...	73·98	10·35	8·56	Full cream.
Goat ...	79·10	4·30	10·44	From skimmed milk.
Handy ...	67·38	0·17	10·20	From skimmed milk.
Home ...	69·44	0·91	9·13	From skimmed milk.
Milkman ...	73·66	11·80	11·40	Warranted to contain all original cream.
Mother ...	70·60	5·57	8·32	From unskimmed milk.
Popular ...	71·75	2·47	10·14	From partly-skimmed milk.
Rose ...	72·40	10·30	9·75	Warranted not skimmed.
Shamrock ...	71·30	—	10·88	From skimmed milk.
St. Olaf ...	71·86	11·30	10·50	From pure unskimmed milk.
Sunlight ...	71·76	5·60	8·63	From unskimmed milk.
Swiss (Nestlé's) ...	75·00	13·50	10·44	From pure milk, and only small quantity of pure cane-sugar.
Swiss (Nestlé's) ...	70·41	11·03	10·51	From pure milk, and only small quantity of pure cane-sugar.
Threepenny ...	66·25	0·30	10·49	From partly-skimmed milk.
Tip-top ...	74·25	8·12	8·82	Warranted not skimmed.
Viking ...	35·16	10·40	9·14	Unsweetened.

NOTE ON THE IODINE AND BROMINE ABSORPTIONS OF
LINSEED-OIL.

BY ROWLAND WILLIAMS.

Iodine Absorption.—The percentage of iodine absorbed by raw linseed-oil, as recorded by different observers, varies considerably, and is, according to my experience, a good deal too low. Thus, in Allen's "Commercial Organic Analysis," vol. ii., p. 50, the original figures of Hübl are quoted as 156 to 160 per cent., whilst Alder Wright ("Oils, Fats, Waxes," p. 183) states the average of a large number of results, obtained by numerous observers and collated by Benedikt, to be 175 per cent.

Allen, in his article on "Fixed Oils and Fats" (Thorpe's "Dictionary of Applied Chemistry," vol. iii., p. 29), gives the iodine absorption as 154 to 160 per cent., although in another part of the same article, while repeating these figures, he mentions the fact that Thomson and Ballantyne (*Journal of the Society of Chemical Industry*, vol. x., p. 233) found considerably higher percentages. The two last-named chemists are, I think, the only observers who have recorded what I have every reason to believe the correct iodine number.

During the last four years I have had exceptional opportunities for the examination of samples representing large bulks of raw linseed-oil (several hundred samples having passed through my hands during that period). Of these, none which I believe to be genuine absorbed less than 180 per cent. of iodine, whilst in the majority of cases the number was nearer 190 per cent., and occasionally exceeded that figure.

I should explain that these figures refer mainly to Baltic linseed-oil, but I have also always found the iodine number of other kinds of linseed-oil (*e.g.*, Indian and River Plate) to be much higher than that usually recorded. Taking at random from my note-book the results of fifty-three samples of Baltic oil, I find the average iodine absorption to be 188.5, and that of six samples of other varieties to be 183.3 per cent. In my determinations I always add a large excess of Hübl's reagent (usually at least double the amount likely to be absorbed), and allow to stand overnight (eighteen to twenty hours), and it is to these two points that I attribute the discrepancy between my figures and those of most other observers. If only a small excess of iodine be employed, and the reaction be permitted to proceed for only four to six hours, as is, I believe, frequently the case, the results obtained will certainly be too low.

Bromine Absorption.—Previously to the appearance of Mr. Hehner's paper on "The Determination of the Bromine Absorption of Fats gravimetrically" (*THE ANALYST*, vol. xx., p. 49), I had not worked in this direction, but since then I have made a large number of bromine absorption determinations, working on the lines suggested by Mr. Hehner. Having convinced myself of the accuracy of this gravimetric method, especially as regards raw linseed-oil, I can confidently recommend it as being in many cases both more convenient and more reliable than the volumetric iodine estimation. It possesses the undoubted advantage of leaving the haloid product in a state suitable for further examination of its physical and other characters if desired. When determinations of the halogen absorptions of oils and fats have to

be made only comparatively rarely, the gravimetric bromine method is certainly to be preferred, as, after one blank experiment to ascertain the freedom of the bromine and chloroform from fixed residue, these reagents are ready for use at a moment's notice. On the other hand, it is essential that Hübl's solution should be fairly newly made, and yet not too new (it is advisable to prepare it at least several hours previous to use), otherwise irregular results will most probably ensue.

Boiled Linseed-oil.—The bromine absorptions of linseed-oil, both boiled and raw (102.4 per cent. and 76 per cent. respectively), as recorded by Mills (Allen's "Commercial Organic Analysis," vol. ii., p. 50), are so obviously wrong as hardly to need correction. Still, it may be interesting to place on record my own observations on this point. It must, however, be remembered that Mills's results were obtained by a colorimetric volumetric process, whereas my own bromine determinations are all gravimetric; so it is perhaps scarcely fair to compare the figures.

On a *priori* grounds one would naturally expect that the thicker the consistency to which linseed-oil has been boiled, viz., the farther removed from its original raw condition, the lower will be its bromine absorption, and *vice versa*. Being in a position where I have special facilities for making gravimetric determinations of the bromine absorption of oil at various stages of boiling on the large scale, I am able to say that this theory always holds good.

In the following table I have recorded the iodine (volumetric) and bromine (gravimetric) absorption figures of a number of samples of linseed-oil, both raw and at different stages of boiling:

	Raw.						BOILED.		
	1.	2.	3.	4.	5.	6.	Thin.	Thin.	Very Stout.
Iodine	183.2%	192.9%	185.2%	195.5%	194.8%	195.1%	175.1%	163.0%	96.9%
Bromine	114.2%	120.7%	115.1%	119.2%	119.6%	119.4%	111.3%	112.4%	59.9%

It will be observed that the ratio between the iodine and bromine figures of raw linseed-oil is very regular, being on the average as 1.62 to 1 (theoretically it should be 1.5875), but in the case of boiled oil the ratio is somewhat irregular.

Examination of Butter. E. Polenske. (*Arch. Gesundheitsw.* ii., 523; through *Zeit. angew. Chem.*, 1895, pp. 581, 582.)—This method is based on the greater solubility of butter-fat in absolute alcohol than of the foreign fats used as adulterants. Twenty-five grammes of the clear butter-fat are weighed into a dry 250 c.c. Erlenmeyer flask, and 125 c.c. of neutral absolute alcohol (specific gravity 0.7963 at 15° C.) added. On warming to about 50° C., and gently shaking, the fat readily dissolves. The flask is then placed in a water-bath maintained at 18° C., being at first loosely corked, but afterwards, when the contents of the flask are also at 18° C., well corked. After an hour the flask is well shaken, the agitation being repeated about ten times at intervals of three minutes. After the contents have stood at 18° C. for one and a half hours in all, 118 c.c. of the alcoholic solution are rapidly filtered through a paper of 10 c.m. diameter, precautions being taken to maintain the temperature as nearly as possible at 18°. The insoluble residue is melted, brought into a flat dish, and, after evaporation of the alcohol, the residue dried for three hours at 100° C. This gives the solid portion of the butter-fat for the investigation. Ten c.c. of the 118 c.c. of the filtrate

are evaporated in a weighed flask, and the weight of the residue multiplied by 11.8 gives the amount of the fluid portion of the butter-fat. The remainder of the filtrate is evaporated, dried, and separately examined, as in the case of the solid fat.

For this method of separation the butter-fat should be as fresh as possible. Five grammes of fat in the fresh condition were neutralized by 1.2 c.c. $\frac{N}{10}$ potash. After being kept three weeks in a cool place there was no appreciable alteration; but after two months the amount of alkali required was 1.8 c.c. At the same time, the solubility in alcohol had risen from 36 to 38.2 per cent.

From the examination of fifty samples of summer and winter butter, the author finds:

1. The limits of the Reichert-Meissl number are closer in the two portions of the fat than in the entire untreated fat. Thus, while with butter-fat the limits are about 8 c.c. apart, in the solid portion this is narrowed to 6 c.c., and in the fluid portion to 5.9 c.c.

2. With a low Reichert-Meissl number the solubility of the fat in alcohol is less.

3. A slight solubility of the fat in alcohol is not always associated with a lower Reichert-Meissl number of the fluid portion.

Experiments made with mixtures of butter with various foreign fats show that by taking the ordinary constants on the fluid portion of the fat more valuable results are obtained than when they are determined on the whole fat. C. A. M.

Acidimetric Estimation of Vegetable Alkaloids. L. F. Kebler. (*Journ. Amer. Chem. Soc.*, xvii., 1895, pp. 822-831.)—This paper is a study of the value of different indicators in the estimation of alkaloids by titration. In the author's opinion, the discordance in the results of different chemists may be largely attributed to the personal equation, each worker arbitrarily assuming his own end-reaction tint. In these experiments the titrations were made from acid to alkaline solutions, and the tints taken for the end-reactions were: Brazil-wood from yellow to onion-red, the purple ultimately fading to this; cochineal from yellow to bluish-red; hæmatoxylin from yellow to brown-orange; litmus from red to onion-red, and methyl-orange from red to straw-yellow.

After testing the value of these by titrating standard acid against a standard alkali, the titration of commercially pure alkaloids was undertaken. In the case of quinine and codeine, 2 grammes of the alkaloid were dissolved in alcohol in a cylinder, and the solution made up to 100 c.c. with alcohol. To 10 c.c. of this, after the addition of the indicator, decinormal acid was added in slight excess, the liquid well agitated, and the excess of acid titrated back with decinormal alkali.

Where the alkaloid was insoluble in alcohol, the two grammes were warmed in a beaker on the water-bath with 75 c.c. of decinormal acid, until the alkaloid dissolved, the solution being then cooled and made up to 100 c.c. with water. Each 10 c.c. then contained 0.2 of a gramme of alkaloid and $7\frac{1}{2}$ c.c. of decinormal acid solution. After adding the requisite amount of indicator to 10 c.c. and diluting to 50 c.c., the excess of acid was determined. Every precaution was taken in preparing the in-

dicators, and the following quantities were used in each case: Cochineal and litmus prepared as described in Sutton's "Volumetric Analysis," the former 5 drops, the latter 10; phenolphthalein, 1 gramme per litre of 50 per cent. alcohol, 5 drops; hæmatoxylin, 1 gramme in 100 c.c. strong alcohol, 3 drops; Brazil-wood solution, 5 drops; methyl-orange, 1 gramme in a litre of distilled water, 5 drops.

The results obtained with several pure alkaloids were:

Indicators.	Quinine.		Strychnine.	Morphine.	Codeine.
	La Wall.	Kebler.			
Brazil-wood ...	99·90	101·97	99·36	98·93	95·75
Cochineal ...	105·56	102·54	103·20	99·08	97·09
Hæmatoxylin ...	99·81	103·37	100·03	98·17	95·90
Litmus ...	101·80	103·55	103·54	98·93	96·38
Methyl-orange ...	—	103·27	104·21	100·59	98·11

The figures in the first column are those obtained by an independent worker.

The following table shows the applicability of the process to crude alkaloids:

Indicators.	Crude Morphine.		Crude Cocaine.
	La Wall.	Kebler.	
Brazil-wood ...	99·23	98·47	95·90
Cochineal... ..	100·14	99·53	97·11
Hæmatoxylin ...	99·08	97·59	95·74
Litmus	99·50	98·93	96·82
Methyl-orange ...	102·10	100·02	100·14

With the same crude morphine the ash method gave 97·59 per cent., the lime-water method 98·22 per cent., and the absolute alcohol method 98·33 per cent. of pure morphine. The crude cocaine yielded, by the gravimetric method of Dr. Squibb (*Ephemeris*, iii., 1171), 97·3 per cent. of nearly pure cocaine.

As it is often necessary to extract the alkaloids from their natural sources, the author has employed a modification of Keller's process for the purpose. To 10 grammes of the dry drug in a 250 c.c. flask, 25 grammes of chloroform and 75 grammes of ether are added, the flask well corked and shaken for some minutes. Ten grammes of 10 per cent. ammonia-water are then added, and the shaking continued at intervals for an hour. On adding 5 grammes more of the ammonia-water, the suspended powder coagulates, and the liquid can be poured off almost completely.

(1) Fifty grammes are evaporated on the water-bath, 10 c.c. of ether added, and again evaporated. The residue is dissolved in 15 c.c. hot alcohol, and water added to slight permanent turbidity. The indicator is then added and an excess of the standard acid solution, which is titrated back with centinormal alkali.

(2) Fifty grammes are shaken with 20 c.c. of acidulated water in a separating funnel, the aqueous solution removed to a second separating funnel, and the shaking repeated twice more with 15 c.c. of slightly acidulated water. The acidulated water in the second funnel is made alkaline with ammonia, and the alkaloid removed successively with 20 c.c., 15 c.c., and 15 c.c. of a mixture of three parts (by volume) of chloroform and one of ether. The residue left on evaporation of the solvents is then treated as in (1) above.

Nux vomica and ipecacuanha-root were treated according to process (1) and (2); belladonna-leaves according to (2). The results were as follows :

	Per Cent. Alkaloids in Nux Vomica by Process (1).		Per Cent. Alkaloids in Nux Vomica by Process (2). Gravimetrically.		Per Cent. Alkaloids in Nux Vomica by Process (2). Volumetrically.		Per Cent. Alkaloid in Ipecac-root by Process (1).	
	La Wall.	Kebler.	La Wall.	Kebler.	La Wall.	Kebler.	La Wall.	Kebler.
Brazil-wood...	2.04	2.58	2.94	3.00	2.37	2.37	2.46	2.54
Cochineal ...	2.64	2.69	2.86	3.10	2.42	2.39	2.59	2.49
Hæmatoxylin	2.18	2.24	2.88	3.11	2.23	2.27	2.48	2.54
Litmus ...	2.38	2.34	2.93	3.05	2.55	2.37	2.55	2.57
Methyl orange	3.02	3.64	2.93	3.02	2.65	2.61	2.95	3.30

	Per Cent. Alkaloid in Ipecac-root by Process (2). Gravimetrically.		Per Cent. Alkaloid in Ipecac-root by Process (2). Volumetrically.		Per Cent. Alkaloids in Belladonna-leaves by Process (2). Gravimetrically.		Per Cent. Alkaloids in Belladonna-leaves by Process (2). Volumetrically.	
	La Wall.	Kebler.	La Wall.	Kebler.	La Wall.	Kebler.	La Wall.	Kebler.
Brazil-wood...	2.58	2.60	2.36	2.35	0.26	0.20	0.19	0.15
Cochineal ...	2.63	2.68	2.52	2.33	0.28	0.20	0.24	0.14
Hæmatoxylin	2.58	2.68	2.35	2.33	0.27	0.22	0.21	0.13
Litmus ...	2.62	2.60	2.40	2.25	0.24	0.18	0.20	0.15
Methyl-orange	2.66	2.63	2.89	2.61	0.25	0.20	0.23	0.20

The nux vomica, examined by the method of Dunstan and Short, showed 2.89 per cent. of crude alkaloid, and this, titrated with acid solution, yielded 2.12 per cent. of pure alkaloid. The figures above show that the Keller process produces an alkaloid residue containing a larger percentage of pure alkaloid.

The conclusions arrived at with regard to the use of the different indicators are :

1. Methyl-orange is unsatisfactory with all strengths of acid, and litmus as ordinarily prepared is also unsuitable.

2. Hæmatoxylin, Brazil-wood, and cochineal give very promising results, hæmatoxylin being the best, and Brazil-wood the next best.

C. A. M.

The Theory of Hübl's Iodine Process, and a Suggestion for its Improvement.
Waller. (*Chem. Zeit.*, 1895, xix., 1786 and 1831.)—The author confirms Hübl's statement that iodine by itself is not completely absorbed by fats. A sample of cotton-oil, heated for an hour to 150° C. with an excess of the reagent, absorbed only 66.6 per cent. The action of nascent iodine is also incomplete. In alcoholic solution the quantity taken up depends on the concentration: one sample of oleic acid (iodine number 93) absorbed 43 per cent. from a 5 per cent. solution, 45 per cent. from one of 10 per cent., 76 per cent. from one of 20 per cent., 78 per cent. from one of 40 per cent., and 82 per cent. from one of 100 per cent. strength. (The presence of the oleic acid increases the solubility of the iodine in alcohol, thus accounting for the possibility of using the two latter solutions.) From 10, 20, and 40 per cent. chloroform solutions, the same oleic acid took up 53, 59, and 59 per cent. of iodine respectively. From 20 per cent. ethereal solution it absorbed 37 per cent., and from a similar solution in carbon bisulphide the absorption was 56 per cent.

A sample of oleic acid (prepared from olive-oil, iodine number 91), treated with

excess of pure bromine, gained in weight an amount equivalent to an iodine number of 95.9. Olive-oil (iodine number 81.55), after being treated twice, gave a number equal to 90.5. An older sample, whose value had fallen from 82 to 73, absorbed the bromine to an amount corresponding to an iodine number of 95.3. It would seem therefore as if the degree of oxidation of an oil might be determined in this manner. The following experiment shows that these high figures obtained on using bromine are not due to substitution. One gramme of olive-oil (iodine number 81.55) was treated for half an hour with 10 c.c. of an 8 per cent. solution of bromine in chloroform; the absorption of bromine was equivalent to 81.45 of iodine. The employment of a solution of potassium bromate and bromide is inconvenient, owing to the lack of a solvent that will withstand the action of the nascent bromine. It might be possible, perhaps, by determining the total bromine used, and also the amount of acid set free during the reaction—converting the latter into bromine, and subtracting it from the total halogen—to attain the desired result.

Experiments were tried with iodine trichloride. Two grammes of oleic acid (iodine number 91) were treated with 1.5 grammes of the chloride; the excess of the halogens was removed, the oil saponified, and the soap ignited. Analysis of the residues gave an iodine number of 94.8.

On an investigation of Hübl's process as ordinarily carried out, it was found that at the end of the operation the whole of the oil was in the chloroform solution, that the chloroform contained both iodine and chlorine, and that the fat contained both halogens in fairly constant quantity. The whole of the mercury (as double iodide) was in the alcoholic layer, and during the absorption free hydrochloric acid was found to be produced, the latter decreasing in amount with the age of the solution, but increasing in proportion to the excess of mercuric chloride used. To this free acid is due the fact that the ordinary iodine number does not correctly express the amount of iodine and chlorine taken up by the fat. It would seem that the nascent chlorine is in part prevented by this free acid from combining with the oil. One gramme of oleic acid (iodine number 91) was treated with the mixed alcoholic solutions of 0.9 gramme of iodine, and 1.08 grammes of mercuric chloride. After decolorization, the liquid was evaporated at 25° to 30° C. to 10 or 15 c.c., till hydrochloric acid vapours appeared. It was diluted with water, extracted with 30 c.c. of chloroform, and thrown on a tared filter. In the filtrate the acid was 0.133 gramme of HCl, or 0.129 gramme of chlorine. The chloroform solution, which contained the greater part of the mercuric iodide precipitated by the water, was passed through the same filter, and the weight of the iodide found to be 1.18 grammes, corresponding to 0.66 gramme of iodine and 0.52 gramme of mercury. From the aqueous liquid, on addition of sulphuretted hydrogen, there was obtained 0.283 gramme of mercury, 0.04 gramme of iodine, and 0.212 gramme of chlorine. The weight of the fatty residue was 1.24 grammes, and contained 0.18 gramme of iodine and 0.057 gramme of chlorine.

The absorption of the halogens by the oil apparently takes place as follows: Some of the iodine is absorbed, and the mercuric chloride is converted into iodide and free chlorine. The water in the alcohol prevents the latter from being taken up by the oil, hence hydrochloric acid is formed and oxygen set free. This then partly combines with that portion of the fat not yet attacked by the halogens, and renders

further action impossible. It follows, from the above, that for every 2 parts of iodine only 1 of mercuric chloride takes part in the reaction. That acid is set free during the process may be proved by comparative titration of the solutions, after decolorization with thiosulphate, by means of decinormal soda and litmus before and after the action on the oil. The amount of acid liberated, even when working on the same fat, is not constant: it varies with the age of the iodine solution, whether the iodine and the mercury are added together or separately, and on the excess of mercury employed. One sample of oleic acid (iodine number 93) gave, with forty-eight days-old iodine, the number 91.65, the free acid being equal to 0.0762 gramme of iodine. In order, therefore, to obtain the *true* iodine number, the latter amount must be subtracted, and the value thus becomes $(91.65 - 7.62)$ 84. The same fatty acid, treated with 0.5 gramme of iodine and 0.48 gramme of mercuric chloride in perfectly fresh solution, gave $(92.1 - 13.9)$ 78.2. (As a check, the halogens in the addition product were determined, and, reckoned as iodine, gave a value of 78.6.) Other tests with increasing amounts of mercuric chloride, the iodine remaining the same, gave lower figures: (1) Using 0.5 gramme of chloride gave $(92.65 - 16.45)$ 76.2, and (2) using 2.0 grammes of chloride $(96 - 24)$, 72.

The falling off of the strength of Hübl's solution is shown by the following experiment: 25 grammes of iodine and 30 of mercuric chloride were dissolved each in 500 c.c. of 95 per cent. alcohol, and the solutions mixed. In five minutes' time the free iodine was 24.7 grammes, and the hydrochloric acid (calculated into iodine) 0.20 gramme per litre. After 85 days, the iodine had fallen to 10.82 grammes, and the acid risen to 14 grammes per litre. This is probably due to the water in the spirit, and not, as stated by Hübl, to the impurities present. It may be obviated to some extent by the use of absolute alcohol, but in the latter case, the small amounts of moisture taken up during the absorption process disturb the results more than when proper allowance is made for the diminished strength of the reagent.

To overcome this difficulty, the author saturates the iodine solution, on preparation, with hydrochloric acid. Twenty-five grammes of iodine are dissolved in 250 c.c. of (95 per cent.) alcohol, 25 grammes of mercuric chloride in 200 c.c. of alcohol added, then 25 grammes of hydrochloric acid, specific gravity 1.19, and the whole made up to 500 c.c. Such a liquid was found, after one hour, to contain 49.31; after 5 days, 49.18; after 20 days, 48.5; and after 64 days, 46.60 grammes of iodine per litre; while the free acid had only risen by an amount equal to 2.54 grammes of iodine. It will be observed that this solution is double the usual strength, but the results obtained agree exactly with those by the ordinary method. The explanation of this must be that the oxygen produced during the action of Hübl's solution is absorbed by the fat only in amount corresponding to the degree with which it still lacks halogen to render it completely saturated. Were this not the case, it would not be evident why the reaction between the iodine and the mercuric chloride should not continue as long as there are unsaturated fatty acids present. The above experiments, however, with varying weights of mercuric chloride, show that it does not so continue.

"Hübl's iodine number," therefore, is in reality the amount, expressed as iodine, of the chlorine, iodine, and oxygen taken up by the fat examined, together with the small amount of chlorine set free from the mercuric chloride by the natural decompo-

sition of the solution during the time of action; while the true iodine number should exclude this latter factor. It is, however, very small in amount, and there seems little reason to substitute for the ordinary process—beyond the improvement suggested above—any method based on the absorption of bromine.

F. H. L.

Quantitative Estimation of Cellulose. Gerhard Lange. (*Zeit. angew. Chem.*, 1895, xix., pp. 561-563.)—In 1889 (*Zeit. phys. Chem.* xiv., 3, p. 283) the author published a method for estimating cellulose, in which the substance was heated with pure alkali and some water to about 150° C. in an oil-bath, the cellulose being subsequently collected, washed, dried, and weighed. Recent experiments have proved that by conducting the operation at the higher temperature of 180° C., a purer cellulose is obtained, containing only a very small amount of nitrogenous matter.

In the amended process a retort is no longer used, but a wide unglazed porcelain crucible, about 65 mm. high. From 5 to 10 grammes of the substance under examination are moistened with a little water in the crucible, and three times the weight of caustic potash (free from nitrate) added, together with about 20 c.c. of water. The crucible is then immersed in an oil-bath, so that the oil is at the same level as the contents of the crucible. The mass is continually stirred with the thermometer from the time frothing commences. As soon as the action has ceased, the crucible is covered with a lid having an opening for the thermometer, maintained at 175° to 180° C. for an hour, and then removed from the oil-bath.

When the temperature has fallen to about 80° C., 75 c.c. of hot water are added, and the mass allowed to cool, after which it is cautiously acidified with sulphuric acid, and washed into a large centrifugal tube. Caustic soda is next added to feebly alkaline reaction, and now nothing but the cellulose remains undissolved.

By energetic whirling in the centrifugal machine the cellulose separates completely and coagulates. The clear liquid is poured off, if necessary through a weighed filter, the cellulose broken up with a glass rod, hot water added, and the tube whirled again. The cellulose is then filtered off, washed with hot water, alcohol, and ether, dried and weighed. The amount of ash is also determined, and this deducted from the weight of the filter and the cellulose gives together the amount of the latter.

With a little practice the estimation can be brought to the drying stage in about two hours and a half.

C. A. M.

The Determination of Tannin by Metallic Oxides. William H. Krug. (*Journ. Amer. Chem. Soc.*, xvii., 1895, pp. 811-814.)—The object of the author's investigation was to discover whether it were possible to substitute a metallic oxide for hide-powder, as used in the ordinary shaking method. The oxides tried were those of mercury, magnesium, zinc, and lead. In each case it was found that after shaking for some time combination was incomplete, and that a further period of standing was necessary to bring this about. This varied considerably with the different oxides. With magnesium and mercury the mixture was ready for filtering after being shaken for four hours and standing all night. With lead oxide two days' standing was required, while zinc oxide stood a week before the absorption of tannin was complete.

The extract used contained 42.35 per cent. soluble solids, and the solution used in the experiments contained 2 grammes of this extract per 100 c.c. Twenty-five c.c. of this dilute extract gave 0.0113 gramme of ash, containing 0.0006 gramme of magnesium oxide.

The tannin was determined by evaporating 25 c.c. of the filtrate, and deducting the dried residue from the weight of the solids in 25 c.c. of the original dilute extract. The ash determinations served to check the amount of oxide dissolved.

EXPERIMENTS WITH ZINC OXIDE.

Method.	Grammes ZnO used.	Diluted Extract used, c.c.	C.c. of Filtrate evapo- rated.	Residue, Grammes.	Per cent. Tannin in Extract.	Ash in Residue, Grammes.	ZnO in Ash, Grammes.
Shaken 4 hours. Stood over-night	2.0	75	25	0.1095	20.45	0.0125	0.0008
Shaken 4 hours. Stood over-night	2.0	75	25	0.1174	18.87	0.0147	0.0019
Shaken 4 hours. Stood a week	2.0	75	25	0.1049	21.37	0.0095	—
Shaken 4 hours. Stood a week	2.0	75	25	0.1029	21.97	0.0103	0.0030
Shaken 4 hours. Stood a week	2.0	75	25	0.1029	21.97	0.0010	0.0020

In the two first cases the filtrate showed a tannin reaction, and in the other three the whole of the tannin was not absorbed until after seven days. For this reason zinc oxide would be valueless where rapid work was required. The results obtained with it were lower than those with lead and mercury oxides, but agreed better with the magnesium oxide figures.

EXPERIMENTS WITH LEAD OXIDE.

Method.	Grammes PbO used.	Diluted Extract, c.c.	Filtrate evapo- rated, c.c.	Residue, Grammes.	Per cent. Tannin in Extract.	Ash in Residue, Grammes.	PbO in Ash, Grammes.
Shaken 3½ hours. Stood 2 days	4.0	75	25	0.0738	27.59	0.0111	0
Shaken 3½ hours. Stood 2 days	4.0	75	25	0.0754	27.27	0.0092	0
Shaken 3½ hours. Stood 2 days	4.0	75	25	0.0706	28.23	0.0105	0

There was no trace of tannin in the filtrates, but the objection to the use of lead oxide is the time required for complete combination.

EXPERIMENTS WITH MAGNESIUM OXIDE.

Method.	Grammes MgO used.	Diluted Extract, c.c.	Filtrate evapo- rated, c.c.	Residue, Grammes.	Per cent. Tannin in Extract.	Ash in Residue, Grammes.	MgO in Ash, Grammes.
Shaken $2\frac{1}{2}$ hours. Stood over-night	2.0	75	25	0.1134	19.67	0.0209	0.0055
Shaken $2\frac{1}{2}$ hours. Stood over-night	2.0	75	25	0.1028	21.79	0.0195	0.0042
Shaken $2\frac{1}{2}$ hours. Stood over-night	2.0	75	25	0.1230	17.75	0.0232	0.0052
Shaken $2\frac{1}{2}$ hours. Stood over-night	2.0	75	25	0.1246	17.43	0.0247	0.0058
Stood 24 hours, with occasional shaking ...	2.0	75	50	0.2063	21.72	0.0252	0.0074
Stood 24 hours, with occasional shaking ...	2.0	75	50	0.2061	21.74	0.0244	0.0076
Stood 24 hours, with occasional shaking ...	2.0	75	25	0.1157	19.21	0.0213	0.0044
Stood 24 hours, with occasional shaking ...	2.0	75	25	0.1114	20.07	0.0205	0.0038
Stood 48 hours, with occasional shaking ...	2.0	75	50	0.1941	22.94	0.0326	0.0064
Stood 48 hours, with occasional shaking ...	2.0	75	50	0.1959	22.76	0.0339	0.0070
Shaken $3\frac{1}{2}$ hours. Stood over-night	2.0	75	50	0.2165	20.70	0.0349	0.0102
Shaken $3\frac{1}{2}$ hours. Stood over-night	2.0	75	50	0.2191	20.44	0.0355	0.0111
Shaken $3\frac{1}{2}$ hours. Stood over-night	2.0	75	50	0.2179	20.56	0.0359	0.0115

The amount of oxide dissolved was considerable, and lowered the tannin correspondingly. Since this error was not constant, no correction for it appeared possible.

EXPERIMENTS WITH MERCURIC OXIDE (YELLOW).

Method.	Grammes HgO used.	Diluted Extract, c.c.	Filtrate evapo- rated, c.c.	Residue, Grammes.	Per cent. Tannin in Extract.	Ash in Residue, Grammes.	HgO in Ash, Grammes.
Stood 48 hours, with occasional shaking ...	4.0	75	25	0.0833	25.69	0.0070	0
Stood 48 hours, with occasional shaking ...	4.0	75	25	0.0829	25.77	0.0077	0
Stood 48 hours, with occasional shaking ...	4.0	75	25	0.0829	25.77	0.0071	0
Shaken $1\frac{1}{2}$ hours. Stood over-night	4.0	75	25	0.0842	25.51	—	—
Shaken 2 hours. Stood over-night	4.0	75	25	0.0867	25.01	—	—

EXPERIMENTS WITH MERCURIC OXIDE (YELLOW) *continued*—

Method.	Grammes HgO used.	Diluted Extract, c.c.	Filtrate evapo- rated, c.c.	Residue, Grammes.	Per cent. Tannin in Extract.	Ash in Residue, Grammes.	HgO in Ash, Grammes.
Shaken 3½ hours. Stood over-night	4.0	75	25	0.0863	25.09	0.0081	0
Shaken 3½ hours. Stood over-night	4.0	75	25	0.0860	25.15	0.0080	0
Shaken 4 hours. Stood over-night	4.0	75	25	0.0839	25.57	0.0084	0
Shaken 4 hours. Stood over-night	4.0	75	25	0.0849	25.37	0.0065	0
Shaken 4 hours. Stood over-night	4.0	75	20	0.0638	26.41	0.0065	0
Shaken 4 hours. Stood over-night	4.0	75	20	0.0692	25.05	0.0103	0
Shaken 4 hours. Stood over-night	4.0	75	20	0.0682	25.29	0.0094	
Shaken 4 hours. Stood over-night	4.0	75	25	0.0863	25.09	0.0083	0
Shaken 4 hours. Stood over-night	4.0	75	25	0.0849	25.37	0.0097	0
Shaken 4 hours. Stood over-night	4.0	75	25	0.0842	25.51	0.0084	0

The foregoing results show that even under variable conditions constant results may be obtained. The end of the reaction may be recognised by the whole mass partially gelatinizing and becoming a dirty brown. The amount of ash held back is fairly constant, and may be neglected. The time required is greater than that with hide-powder, but the uniform results obtained compensate for this.

C. A. M.

The Analysis of Lead: Metal and Ores. H. Nissenson and B. Neumann. (*Chem. Zeit.*, 1895, xix., 1141-1143.)—*Soft Lead.*—For a proper valuation of this material, more especially when it is to be used for the manufacture of pigments, it is necessary to determine the whole of the impurities present. The following scheme includes silver, copper, bismuth, cadmium, zinc, iron, nickel and cobalt, tin and antimony (arsenic and manganese being very seldom detected). 200 grammes of the metal in small pieces are put into a 2-litre flask with 1275 c.c. of water, 325 c.c. of nitric acid (sp. gr. 1.4) are added, and the whole warmed on the sand-bath till dissolved. The liquid is cooled and the lead precipitated with 62 c.c. of strong sulphuric acid. It is not necessary to allow the precipitate to settle for a long time (*cf.* Fresenius), as modern soft lead only contains antimony to the third place of decimals of a per cent., nor need hydrochloric acid be added to throw down the silver. After cooling the liquid is made up to 2 litres, well shaken, and when again clear 1750 c.c. are filtered off and evaporated to dryness in a porcelain basin. The residue is treated with a little water, filtered and washed. The insoluble portion is digested in an Erlenmeyer flask with caustic

soda and 25 c.c. of cold saturated sodium sulphide solution to dissolve the antimony, and the liquid (A) is filtered off to be subsequently added to the bulk of the antimony. The main filtrate, which if not acid is made so with a few drops of hydrochloric acid, is treated with sulphuretted hydrogen till the liquid becomes perfectly clear, and is separated into a precipitate (C) and a filtrate (D). To C 25 c.c. of sodium sulphide are added, which dissolves the antimony, tin, and arsenic. In the absence of arsenic, the dissolved portion is mixed with A, made up to 200 c.c. and electrolyzed at the boil in a platinum basin for half an hour with a current of 1.2 ampères and 2 volts ($N.D_{100} = 1.2$ ampère), to remove the *antimony*. The *tin* is estimated either by destroying the sodium sulphide with 25 grammes of solid ammonium sulphate and electrolyzing for twenty minutes, or the solution may be acidified with dilute sulphuric acid and the tin sulphide ignited gently, moistened with nitric acid and weighed as oxide. In the presence of arsenic the solution containing the three sulphides must be acidified with weak sulphuric acid, the *arsenic* removed from the precipitate by cold ammonium carbonate (to be estimated either as sulphide or as ammonio-magnesium arseniate) and the antimony and tin dissolved in sodium sulphide and separated as above.

The insoluble portion of C is boiled with aqua regia, the silver chloride removed, the liquid evaporated to dryness with a little sulphuric acid to get rid of the lead, the residue taken up in water, and ammonia and ammonium carbonate added. The precipitate of *bismuth* is filtered off, dissolved in nitric acid, evaporated in a tared basin and weighed as Bi_2O_3 . In the solution is dissolved 1 gramme of potassium cyanide, and the *cadmium* thrown down with a few drops of sodium sulphide, to be treated like the bismuth precipitate. The potassium cyanide is then destroyed by boiling with sulphuric acid, the solution diluted to 200 c.c., and the *copper* deposited on a small and light electrode by a current of 1.1.5 ampère and 2.5.3 volts passing for one to two hours. The acid liquid may also be treated with 0.5 gramme of solid sodium thiosulphate, and the copper sulphide weighed as oxide.

The liquid D is boiled till it becomes cloudy, oxidized with bromine-water, and caustic soda added. The precipitation is repeated a second time to ensure all the zinc remaining dissolved. The precipitate is dissolved in dilute sulphuric acid, and the *iron* thrown down twice with ammonia, and determined volumetrically with permanganate. The filtrate is made alkaline with ammonia, 25 grammes of ammonium sulphate added, and the *cobalt* and *nickel* recovered by an electric current of 1.5 ampère, 2.5.3 volts for half an hour. The alkaline *zinc* solution is acidified, excess of ammonia added, made up to 500 c.c., and titrated by Schaffner's method with sodium sulphide, using lead-paper as an indicator.

The *silver* is determined in a special portion of the metal by cupellation, and the lead is estimated by difference. All the above results are calculated on 179.12 grammes of lead, as the original precipitate of sulphate occupies 46 c.c. (1954 : 200 :: 1750 : 179.12).

Hard or Antimonial Lead.—Here it is only necessary, as a rule, to estimate the antimony and the copper. Fresenius' method for the former (*Quant. Anal.*, ii., 483) is objectionable, owing to the repeated filtrations required; and the fusion processes are tedious. 2.5 grammes of the alloy, 10 grammes of tartaric acid, 15 c.c. of water,

and 4 c.c. of 1.4 nitric acid, are put into a 250 c.c. flask and dissolved. 4 c.c. of strong sulphuric acid are added, and when cold made up to the mark. The lead sulphate is perfectly free from antimony. 50 c.c. of the filtrate are made strongly alkaline with caustic soda, 50 c.c. of sodium sulphide added, boiled, filtered immediately, and the liquid electrolyzed hot for an hour to yield the *antimony*. The *copper* may be obtained from the undissolved portion either by electrolysis or determined by colorimetry.

Commercial leads are dissolved as above, from 5-10 grammes of tartaric acid being added to the solution of 10-50 grammes of the metal. The lead is precipitated with 3 c.c. of strong sulphuric acid for each 10 grammes of lead, and if only a portion of the liquid is taken for analysis, the same allowance of 2.15 c.c. (*sic cf. ante*) per 10 grammes of metal is made. The solution is concentrated, treated with caustic soda and sodium sulphide, and the dissolved antimony, arsenic and tin treated as above. The residue is dissolved in aqua regia, evaporated to dryness, dissolved in hydrochloric acid, filtered from the silver and treated with sulphuretted hydrogen. Both precipitate and filtrate are treated as before. When it is required only to know the amount of silver, copper and antimony present, the following method suffices: The silver is determined by cupellation, the antimony by electrolysis, and the residue insoluble in sodium sulphide is dissolved in aqua regia, supersaturated with ammonia and the copper determined colorimetrically, care being taken that the liquid for examination contains not more than 1 per cent. of copper.

Galena.—It is often necessary only to determine the lead, silver, arsenic and zinc in this material. The silver is estimated as before, but the lead is determined directly (especially when antimony and copper are present). 0.5 gramme is dissolved in 30 c.c. of 1.4 nitric acid, diluted, and electrolyzed hot in a platinum basin with a current of 1-1.5 ampère, 2.5 volts ($N.D_{100} = 1$ ampère), the basin itself being the anode. The peroxide is dried at 180° C. and weighed. For the arsenic, 1 gramme is dissolved, evaporated with sulphuric acid, diluted and filtered. To the filtrate, 5 grammes of tartaric acid, 30 c.c. of ammonia, 15 c.c. of magnesia mixture are added. The precipitate is allowed to settle, filtered off, dissolved in nitric acid, run into a porcelain basin, evaporated and ignited (phosphoric acid is never present). For the zinc, 2 grammes are boiled with hydrochloric acid till all the sulphuretted hydrogen is driven off, 5 c.c. of nitric and 8 c.c. of dilute sulphuric acid added, and the whole evaporated to half the volume. The liquid is diluted, 50 c.c. of ammonia added, boiled, and when cold made up to 500 c.c. Half the liquid is taken and titrated with sodium sulphide as above.

In the case of sulphides of lead and copper containing silver, etc., the two metals cannot be separated directly by electrolysis; the lead is thrown down as above, the peroxide remaining in the acid liquid for a few moments after the current has ceased, to free it from traces of copper; then the liquid is evaporated with sulphuric acid to dryness, dissolved in water, and the copper precipitated with thio-sulphate.

F. H. L.